

blast treatment, a flame treatment, a corona treatment, a plasma treatment, a sputter etching treatment, a radiation irradiation treatment, and the like. Of these, the corona treatment is able to produce, on the fluorine resin surface, various types of functional groups that contribute to imparting good bonding properties thereto and is thus known as an effective treating method.

However, the fluorine resin surface treated by these treating methods may be unsatisfactory, in some cases, with respect to its bonding force, thus the best use being not made of the surface-treating effect at present.

On the other hand, with regard to the crosslinking elastic adhesive body, an attempt has been made to formulate a silane coupling agent for the purpose of improving the quality of the resin.

However, the present inventor has found that the crosslinking elastic adhesive body formulated with a silane coupling agent is disadvantageous in that its properties of bonding to the surface-treated fluorine resin are poor. Accordingly, there is a demand of solving this problem.

SUMMARY OF THE INVENTION

Under these circumstances in the art, the present invention has for its first object the provision of a method for the surface treatment of a fluorine resin, which is suitable for reliably making a laminate obtained by direct and strong bonding between a fluorine resin and a crosslinking elastic adhesive body, such as of an ethylene-vinyl acetate copolymer or the like, and also a method for making a laminate. The invention has as its second object the provision of a laminate in which a fluorine resin and a crosslinking elastic adhesive body, such as of an ethylene-vinyl acetate copolymer or the like, are directly, strongly bonded together and which is excellent in initial bonding property and storage stability, and also of a method for making the laminate.

To achieve the above objects, the present inventor has made intensive studies, and as a result, found, as a measure for achieving the first object, methods (1) to (3) set out below, a fluorine resin treated by the methods, and a method for making a laminate having the fluorine resin therein.

(1) A method for the surface treatment of a fluorine resin wherein the surface of the resin has an absorbance at 360 nm of not smaller than 0.02/100 cm² when measured by iodometry.

(2) A method for subjecting a fluorine resin surface to corona discharge treatment in an atmosphere of a nitrogen gas while controlling the concentration of an oxygen gas to 4 to 150 ppm.

(3) A method for carrying out a thermal treatment after having subjected a fluorine resin surface to corona discharge treatment in air.

With respect to the method (1), there have been initially investigated acidic or reductive functional groups and radical-generating function groups (a diazo group, a peroxide and the like) that are produced on the surface treatment of a fluorine resin. As an index indicating strong bond with a crosslinking elastic adhesive body upon crosslinkage, there has been studied a peak of I₃⁻ detected at 360 nm in an iodometric method evidencing the existence of the functional groups (i.e. a method set out in known literature including "Chemistry of Organic Peroxides", edited and written by Yoshiro Ogata, Nanko-Do p. 331 (1971), Jane E. Flew, et al., Analytica Chimica Acta, 155, p. 139 (1983), Organic Synthetic Chemistry, by Masayuki Yoshida, 27. P.257 (1969), etc).

As a consequence, it has been found that a fluorine resin, which is so treated that its absorbance at 360 nm is detected as a value of 0.02/100 cm² or over, preferably 0.03/100 cm² or over, is excellent in the bonding property as a whole. When the thus treated fluorine resin and a crosslinking elastic adhesive body, such as of an ethylene-vinyl acetate copolymer or the like, are directly laminated

A surface-treating method of a fluorine resin, a method for making a laminate, and a laminate according to the embodiments of the invention are summarized below.

According to one embodiment of the invention, there is provided a method for surface-treating a fluorine resin, which comprises surface-treating a surface of a fluorine resin sheet so that the surface has an absorbance at 360 nm of not lower than 0.02/100 cm² when determined by iodometry. The absorbance is preferably at 0.03/100 cm² or over.

The surface treatment is preferably carried out by corona discharge treatment of the fluorine resin surface while controlling a concentration of an oxygen gas at 4 to 150 ppm in a nitrogen gas atmosphere. In this case, the oxygen gas concentration is preferably in the range of 4 to 50 ppm.

According to another embodiment of the invention, there is also provided a method for surface-treating a fluorine resin, which comprises subjecting a surface of a fluorine resin to corona discharge treatment in air, and thermally treating the thus-treated resin.

The thermal treatment is preferably carried out at a temperature of 80 to 300°C for 5 to 60 minutes. In all the embodiments set out above, the fluorine resin consists of an ethylene-tetrafluoroethylene copolymer.

According to a further embodiment of the invention, there is provided a method for making a laminate wherein a fluorine resin and a crosslinking elastic adhesive body are directly bonded together, which method comprising laminating the crosslinking elastic adhesive body to a fluorine resin surface, which has been treated according to one of the following methods (1) to (3):

(1) the fluorine resin surface is so treated that its absorbance at 360 nm is 0.02/100 cm² or over when determined by iodometry;

(2) the fluorine resin surface is treated with corona discharge in an atmosphere of a nitrogen gas while

Fig. 7

Fig. 7 is an illustrative view showing a peeling test of laminate 3.

DETAILED EMBODIMENTS OF THE INVENTION

The invention is now described in detail. The surface-treating method of a fluorine resin, which is a measure for achieving the first object of the invention, is a surface treatment for strongly bonding a fluorine resin and a crosslinking elastic adhesive body. The fluorine resin is treated by one of the following methods (1) to (3):

(1) a surface-treating method wherein the fluorine resin surface is treated so that its absorbance at 360 nm is at 0.02/100 cm² or over when determined by iodometry;

(2) a method wherein the fluorine surface treatment is subjected to corona discharge treatment while controlling a concentration of an oxygen gas in an atmosphere of nitrogen gas ranges from 4 to 150 ppm; and

(3) a method wherein the fluorine resin surface is treated with corona discharge in air and subsequently thermally treated.

The fluorine resin treated according to one of the methods (1) to (3) is not critical in type and includes, for example, polytetrafluoroethylene (PTFE), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), tetrafluoroethylene-perfluoroalkylvinyl ether copolymer (PFA), polychlorotrifluoroethylene (PCTFE), polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF), ethylene-tetrafluoroethylene copolymer (ETFE), ethylene-chlorotrifluoroethylene copolymer (ECTFE), and the like. These may be appropriately selected depending on the end use of the laminate using a treated fluorine resin.

In the practice of the invention, it is preferred to use an ethylene-tetrafluoroethylene copolymer, which is thermoplastic in nature and is excellent in moldability, heat resistance, resistance to chemicals, electric characteristics (dielectric characteristic), non-

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adhesiveness, abrasion resistance, cut-through resistance, radial ray resistance, UV transmission, IR absorptivity and the balance of these characteristic properties. Accordingly, the copolymer can be conveniently used as a surface material
5 for outdoor electric members.

To optimize the property of bonding to a crosslinking elastic adhesive body, the surface-treating method (1) of a fluorine resin according to the invention comprises treating the fluorine resin in such a way that its absorbance is
10 0.02/100 cm² or over when determined by iodometry.

In the treating method (1), the absorbance at 360 nm, at which a peak of I₃⁻ is obtained at the surface thereof according to an iodometric method, is adopted as an index indicating the quantity of radical-generating functional
15 groups (an azo group, a peroxide), and the absorbance should be 0.02/100 cm² or over, preferably 0.03/100 cm² or over. If the absorbance is less than 0.02/100 cm², the amount of the radical-generating functional groups is too small to impart satisfactory bonding to a crosslinking elastic adhesive body.

The above measuring method may be ones that are set out in the afore-mentioned known literature ("Chemistry of Organic Peroxides", edited and written by Yoshiro Ogata, Nanko-Do p. 331 (1971), Jane E. Flew, et al., Analytica
20 Chimica Acta, 155, p. 139 (1983), Organic Synthetic Chemistry, by Masayuki Yoshida, 27. P.257 (1969), etc).

In the present invention, so far as such an absorbance as defined above at the surface of the fluorine resin is ensured, there may be used various surface-treating methods including, for example, corona treatment, flame treatment,
30 low pressure plasma treatment, atmospheric pressure plasma treatment, UV irradiation treatment, laser irradiation treatment, electron beam irradiation treatment, radiation irradiation treatment and the like. In the practice of the invention, the corona treatment is preferred.

The corona treatment may be one that is known in the art and includes a method, which is carried out in an atmosphere of nitrogen gas at a low concentration of oxygen
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gas. For reducing the concentration of oxygen gas to a low level, mention is made of methods including a method, in which a gas other than oxygen gas is blown at an atmospheric pressure at a portion where a corona discharge takes place, a method, in which a corona discharge portion is covered such as with a polymer sheet, and after sealing, an inner gas is replaced by a gas other than oxygen, and a combination thereof. Gases other than oxygen include nitrogen, argon, carbon dioxide, helium, tetrafluoromethane and the like, of which nitrogen gas is preferred because of its inexpensiveness with no danger. It will be noted that the oxygen concentration can be measured, for example, by a galvanic cell type densitometer.

According to the method of (1), the fluorine resin can be surface-treated so as to ensure direct, strong bonding to a crosslinking elastic adhesive body.

Next, the treating method (2) is one wherein a fluorine resin can be strongly bonded to a crosslinking elastic adhesive body and is imparted with a good bonding property along with good storage stability.

In the treating method (2) of the invention, when the fluorine resin is subjected to corona discharge treating under given conditions, it is necessary to control a concentration of an oxygen gas in a nitrogen gas atmosphere at a given very low level. The oxygen concentration is generally in the range of 4 to 150 ppm, preferably 4 to 100 ppm, and more preferably 4 to 50 ppm. If the oxygen concentration is less than in the above range, storage stability becomes worsened when a laminate is fabricated. On the other hand, when the concentration exceeds the range, an initial bonding force considerably lowers.

The procedure of controlling the oxygen gas concentration at a very low level includes those methods including, for example, a method, in which a nitrogen gas is blown, at an atmospheric pressure, against a portion where corona discharge takes place, a method, in which a corona discharge portion is covered with a polymer sheet or the